PRAXAIR

Advanced Hydrogen Liquefaction Process

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Joe Schwartz
Praxair - Tonawanda, NY

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DOE Hydrogen Program

Project ID
PDP-31

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Introduction

2008 Budget

	Requested	Spent Through 4/15/08
DOE	$ 99,712	$ 0
Praxair	$ 24,928	$ 0
TOTAL	$124,640	$ 0

Program Timeline

7/08 - 7/09	7/09-7/10	7/10-7/11
Phase I	Phase II	Phase III
1 2	3 4	5 6

- **Phase I - Feasibility**
  1 Develop Alternative Hydrogen Liquefaction Processes
  2 Validate Ortho-Para Conversion Process Performance
- **Phase II - Hydrogen Liquefaction Process Development**
  3 Establish Efficiency, Equipment, and Material Performance Targets
  4 Estimate Capital Cost
- **Phase III – Process Performance Evaluation**
  5 Demonstrate Improved Ortho-Para Conversion Process
  6 Evaluate Potential Cost Reduction and Efficiency Improvement

Barriers Addressed

- **C. High Cost and Low Energy Efficiency of Hydrogen Liquefaction**
  - Reduced capital cost
  - Improved efficiency
  - Improved overall process by integration

Objectives

- **Program - Develop a low-cost hydrogen liquefaction system for 30 and 300 tons/day that meets or exceeds DOE targets for 2012**
  - Improve liquefaction energy efficiency
  - Reduce liquefier capital cost
  - Integrate improved process equipment invented since last liquefier was designed
  - Continue ortho-para conversion process development
  - Integrate improved ortho-para conversion process
  - Develop optimized new liquefaction process based on new equipment and new ortho-para conversion process
- **Phase I – Feasibility**
  - Develop conceptual designs for improved processes
  - Validate ortho-para conversion process performance

Hydrogen Liquefaction Targets

Category	2005 Status	2012	2017
Small-Scale Liquefaction (30,000 kg H_2/day)			
Installed Capital Cost ($)	$50M	$40M	$30M
Energy Efficiency (%)	70%	75%	85%
Large-Scale Liquefaction (300,000 kg H_2/day)			
Installed Capital Cost ($)	$170M	$130M	$100M
Energy Efficiency (%)	80%	>80%	87%

$$\text{Efficiency} = \frac{\text{Liquefied Hydrogen LHV}}{\text{Liquefied Hydrogen LHV + Liquefaction Energy}}$$

Milestones

- **Phase I - Feasibility**
  - Develop Novel Conceptual Process Designs
  - Validate Improved Ortho-Para Performance
- **Phase II - Process Development**
  - Establish Performance Targets
  - Develop Preliminary Capital Cost Estimate
- **Phase III – Performance Evaluation**
  - Demonstrate Ortho-Para Performance
  - Validate Capital Cost and Performance Improvement

Program Approach

- **Build on successful high-risk, low-effort program funded through EMTEC**
  - $200,000 program that demonstrated potential for improved ortho-para conversion process
  - Enabled Praxair to propose this project to advance hydrogen liquefaction process development
- **Incorporate other process improvements beyond improved ortho-para conversion**

Phase I Plan

- **Process Optimization, Design, and Economics (45%)**
  - Develop alternative hydrogen liquefaction processes that can optimally integrate new equipment and improved ortho-para process
- **Process Equipment Evaluation (30%)**
  - Evaluate commercially available critical equipment
  - Evaluate novel turbomachinery
- **Ortho-Para Conversion Optimization (25%)**
  - Validate process performance in laboratory-scale test facilities

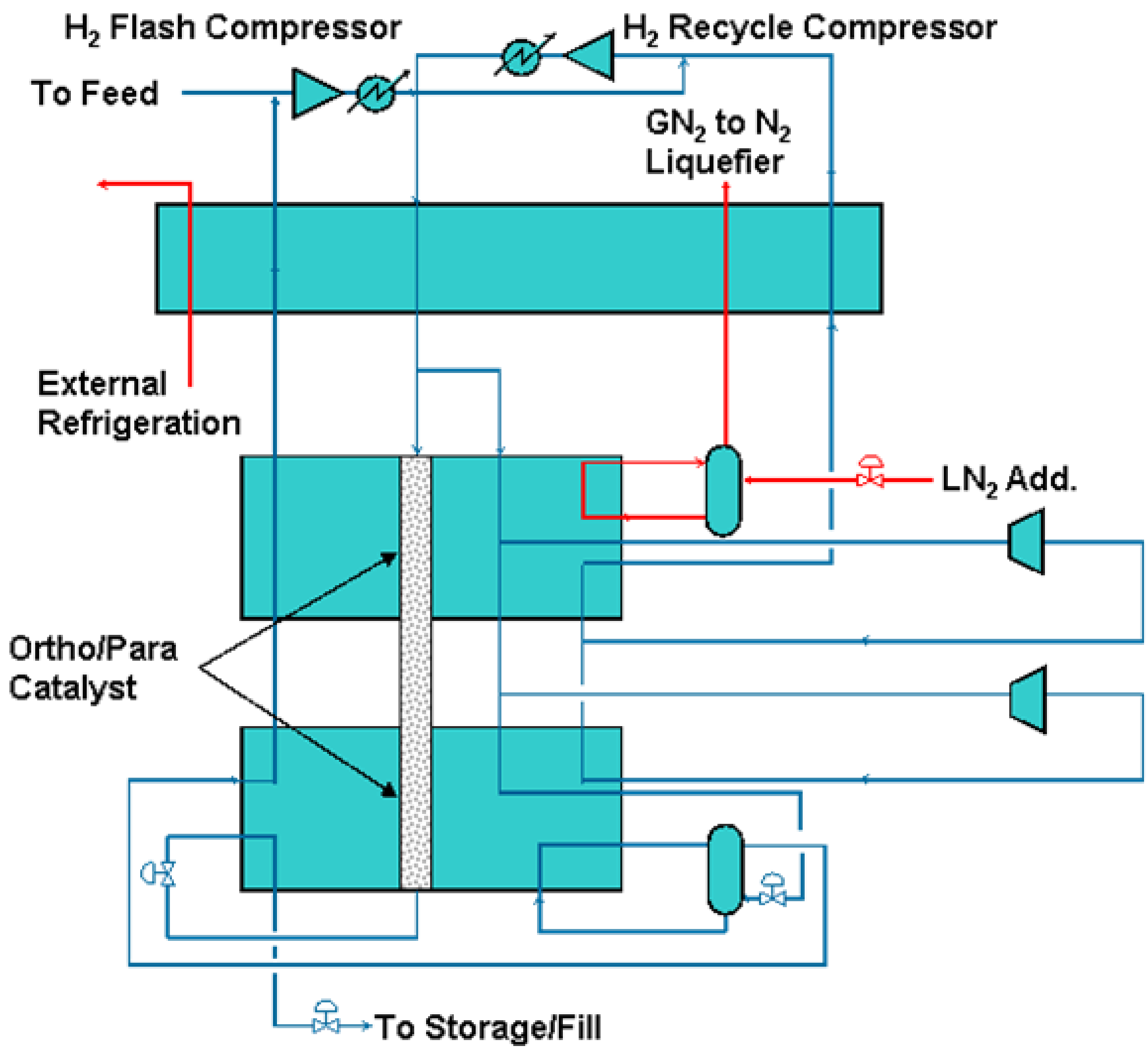
Liquid Hydrogen

- **In the 1960's, liquid hydrogen plants were built to support the Apollo program**
  - Space shuttle capacity is 113 tons (383,000 gallons)
  - Saturn V rocket used 100 tons (339,000 gallons)

Photo courtesy of NASA

- **Today, liquid hydrogen is used to reduce the cost of hydrogen distribution**
  - Liquid hydrogen can be transported economically in larger quantities for longer distances than compressed gas
  - Liquid hydrogen is used to provide high purity product because impurities condense before hydrogen

Hydrogen Liquefaction
Existing Process Flow Diagram



Hydrogen Liquefaction

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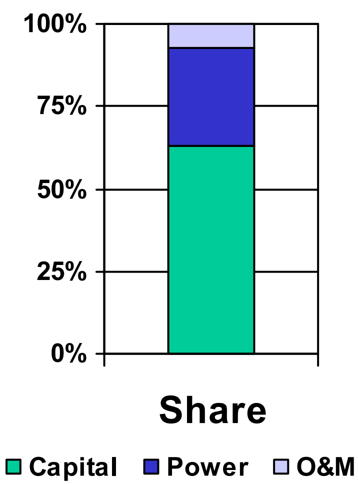
- **The plants are very capital intensive**
  - Infrequent builds make it difficult to reproduce designs
  - Large plants have high capital risk
    - Want to avoid unused capacity
- **The process is very energy intensive**
  - Typical unit powers are about 12.5 to 15 kWh_e/kg
  - Hydrogen lower heating value is about 33 kWh/kg
  - Hydrogen boiling point is 20 K = - 253ºC = - 423ºF
- **Capital cost is more than half of the total**



Hydrogen Distribution

Liquid Tanker

4500 kg H_2

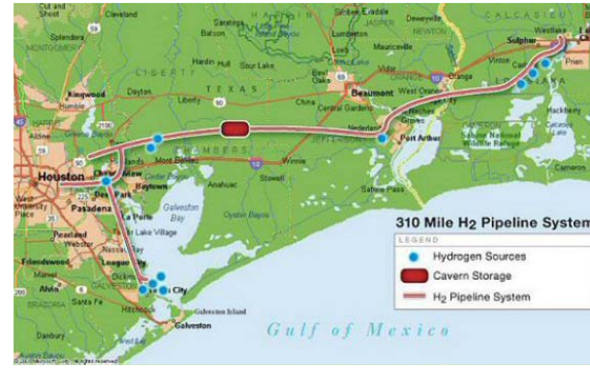
Tube Trailer

300 kg H_2

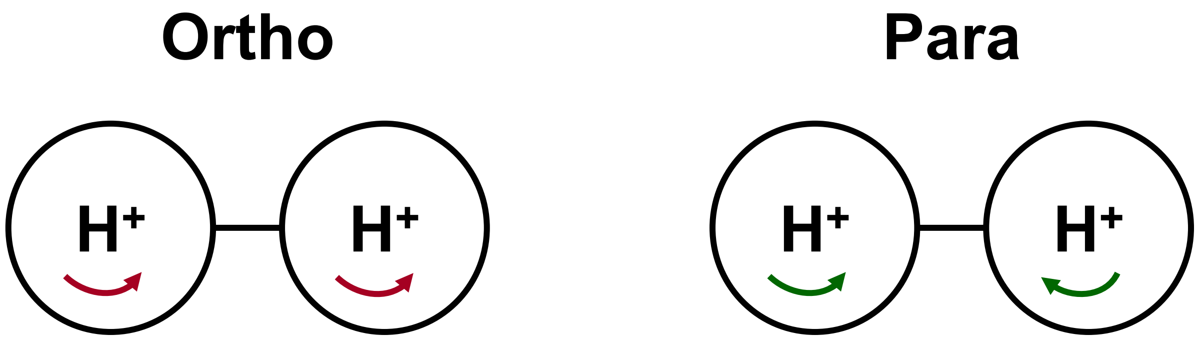
- **Both weigh about 80,000 lbs**
- **Liquid hydrogen might not be the best way to supply the "Hydrogen Economy", but it will play a significant role in the transition period**

Hydrogen Delivery

- Pipeline (~ 1 billion scfd)
  - Refineries and other large hydrogen consumers
- Liquid (~ 10 million scfd)
  - 1.8 million scf/truck
  - Liquid serves an important market segment
- Tube Trailers
  - 125,000 scf/truck
- Cylinders
  - 250 scf/cylinder



Forms of Molecular Hydrogen

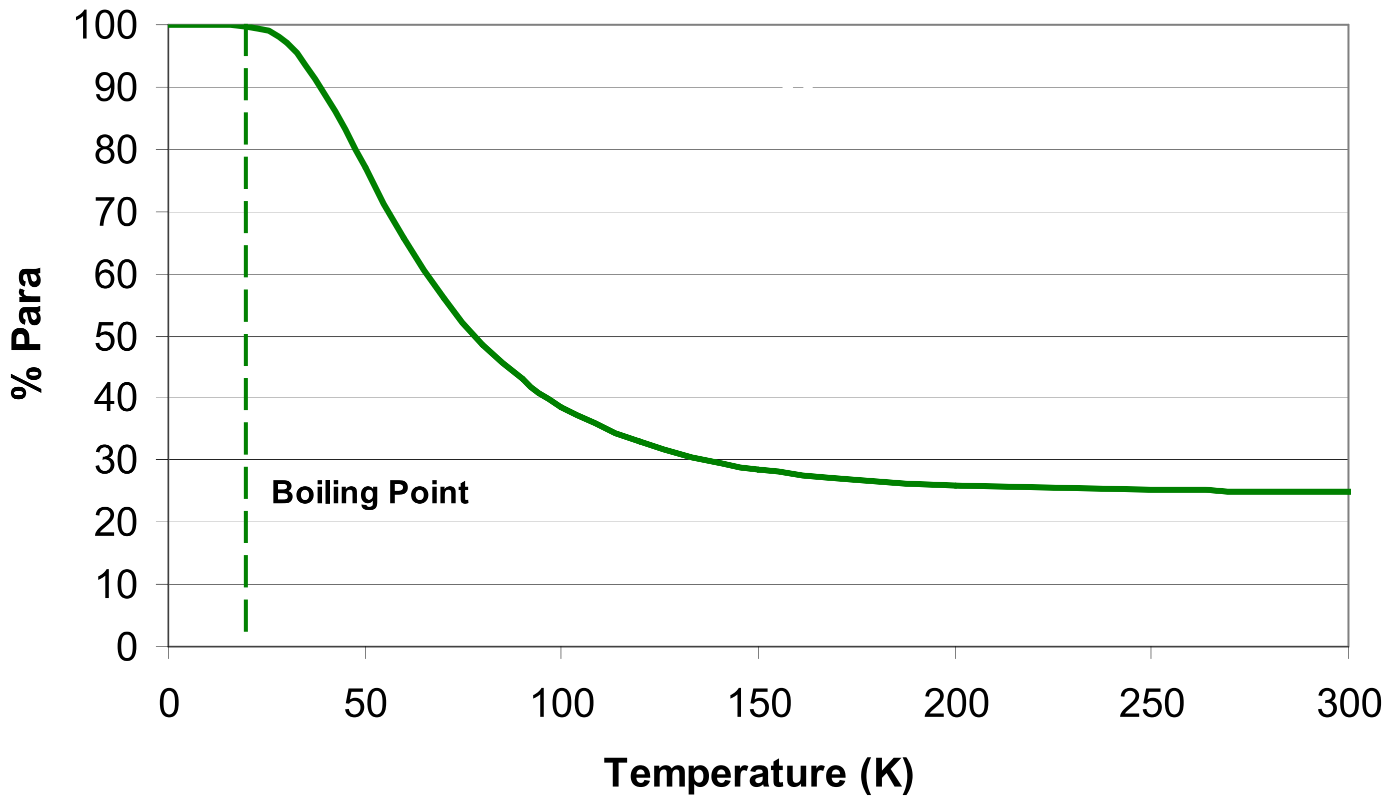


- **Difference is due to proton spin**
  - Normal Hydrogen is 75% Ortho, 25% Para
  - Equilibrium Liquid Hydrogen is 0.2% Ortho, 99.8% Para

- **Ortho-Para conversion requires 18 - 45% of the minimum work requirement for liquefaction***
  - Depends on the conversion process used

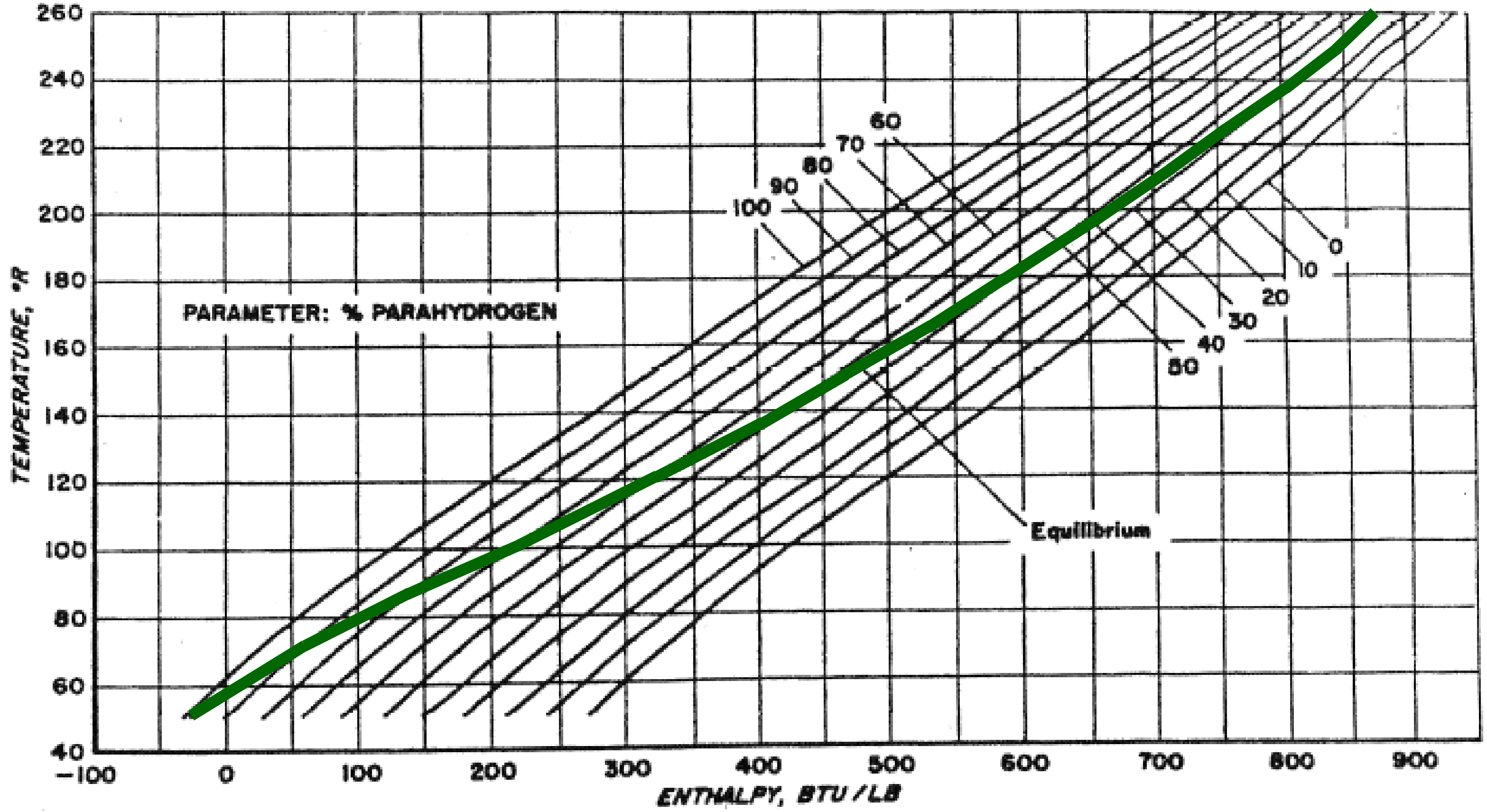
* From Baker, C. R. and Shaner, R. L. *A Study of the Efficiency of Hydrogen Liquefaction,* Int. J. Hydrogen Energy, v. 3, p. 321, 1978.

Equilibrium Composition



- **Para fraction increases as temperature approaches liquid range**
  - Catalyst is used to reach equilibrium composition during cooling

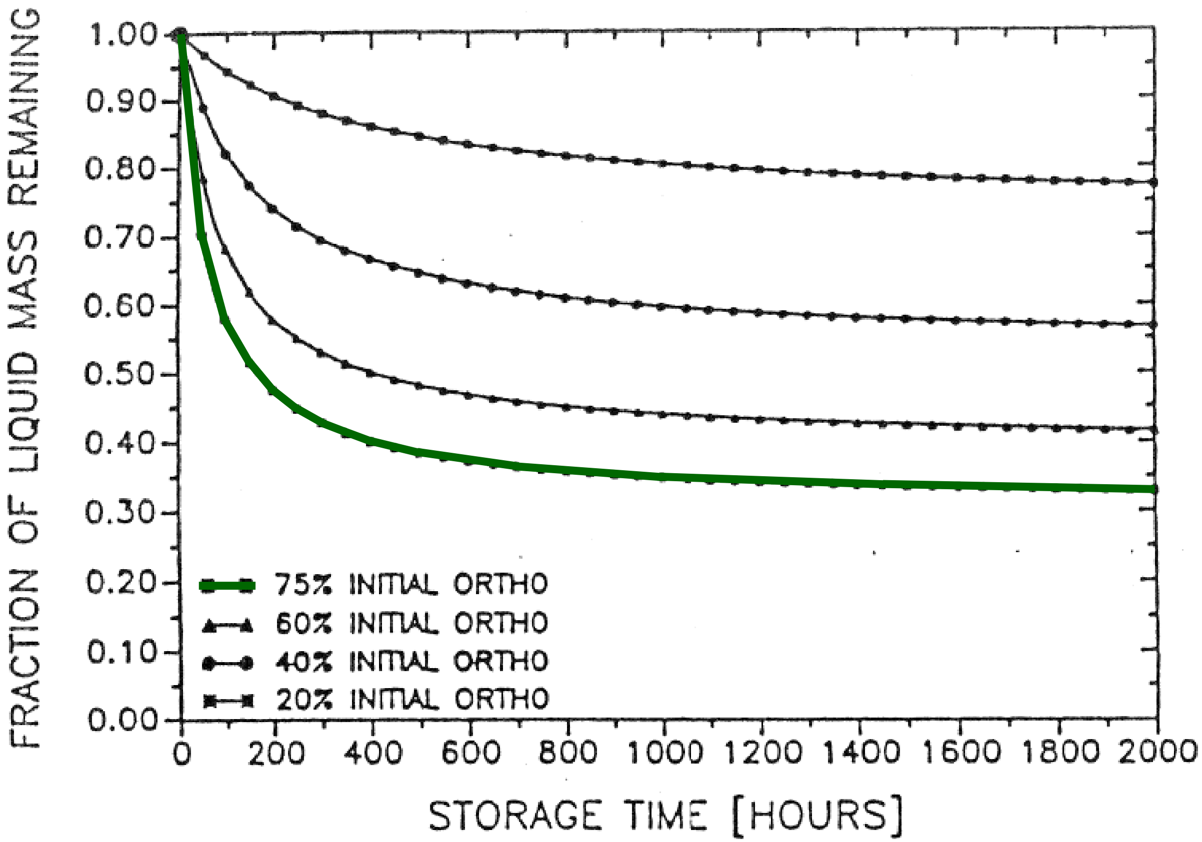
Ortho-Para Enthalpy



- **Heat of liquefaction/vaporization is 192 Btu/lb**
- **Heat of conversion from n-H_2 to e-H_2 in liquid is higher**

From Singleton, A. H. and Lapin, A. *Design of Para-Orthohydrogen Catalytic Reactors,* Adv. Cryo. Eng., v. 11, p. 617, 1965.

Boil-Off Loss



- **Heat of conversion from normal to para is higher than the heat of liquefaction**
  - Spontaneous conversion in the storage tank can cause vaporization

Calculated values from:

Gursu, S. et al. *An Optimization Study of Liquid Hydrogen Boil-Off Losses,* Int. J. Hydrogen Energy., v. 17, p. 227, 1992.

Future Work – Task 1

- **Process Optimization, Design, and Economics**
  - Develop alternative liquefaction processes
    - 2009 Critical Milestone
  - Incorporate improved ortho-para conversion process
  - Estimate capital cost
    - 2010 Critical Milestone
  - Establish component performance targets
    - 2010 Critical Milestone
  - Develop process simulations for new designs
  - Validate potential cost reduction
    - 2011 Critical Milestone

Future Work – Task 2

- **Process Equipment Evaluation**
  - Evaluate commercially available critical equipment
    - Use this to develop new liquefaction processes
  - Evaluate novel turbomachinery
    - Use this to develop new liquefaction processes
  - Estimate capital cost
    - 2010 Critical Milestone
  - Update critical equipment evaluation

Equipment development is beyond the scope of this program

Future Work – Task 3

- **Ortho-Para Conversion Process Optimization**
  - Validate improved ortho-para performance
    - 2009 Critical Milestone
  - Select best candidate ortho-para process
  - Demonstrate process performance
    - 2011 Critical Milestone

Hydrogen Liquefier
Equipment Design Considerations

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Component	State of the Art	Near Term	Long Term
Compressors	Reciprocating Screw	Reciprocating Centrifugal	Centrifugal Hydride Shockwave
Pre-Cooling	Liquid N_2	Mixed gas	Magnetic
Low-Temp Refrigeration	Reverse Brayton	Reverse Brayton with advanced turbines	Magnetic Acoustic
Heat Exchangers	Brazed aluminum	Brazed aluminum Micro-channel	Micro-channel
Ortho-Para Conversion	Catalytic conversion	Improved ortho-para process	Advanced ortho-para process

Summary

- Multi-faceted approach to improving hydrogen liquefaction by improving process efficiency and reducing capital cost
- Goal is to define a new liquefaction process that integrates state-of-the-art equipment and takes full advantage of its increased capability
- Incorporate improved ortho-para conversion process already under development